



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification <sup>7</sup> : C08G 63/88, B01D 9/00</p>	<p>A1</p>	<p>(11) International Publication Number: WO 00/68294</p> <p>(43) International Publication Date: 16 November 2000 (16.11.00)</p>						
<p>(21) International Application Number: PCT/EP00/04399</p> <p>(22) International Filing Date: 9 May 2000 (09.05.00)</p> <p>(30) Priority Data:</p> <table border="0"> <tr> <td>09/309,923</td> <td>11 May 1999 (11.05.99)</td> <td>US</td> </tr> <tr> <td>09/309,921</td> <td>11 May 1999 (11.05.99)</td> <td>US</td> </tr> </table> <p>(71) Applicant: SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V. [NL/NL]; Carel Van Bylandtlaan 30, NL-2596 HR The Hague (NL).</p> <p>(72) Inventors: CHEN, Ye-Mon; 2215 Bent River Drive, Sugar Land, TX 77479 (US). COREY, Ann, Marie; 575 Letch- worth Drive, Akron, OH 44303 (US). DUH, Ben; 768 Jen- nifer Trail, Tallmadge, OH 44278 (US).</p>		09/309,923	11 May 1999 (11.05.99)	US	09/309,921	11 May 1999 (11.05.99)	US	<p>(81) Designated States: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p>Published</p> <p><i>With international search report.</i></p> <p><i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>
09/309,923	11 May 1999 (11.05.99)	US						
09/309,921	11 May 1999 (11.05.99)	US						
<p>(54) Title: PROCESS AND APPARATUS FOR THE CRYSTALLISATION OF POLYTRIMETHYLENE TEREPHTHALATE</p> <p>(57) Abstract</p> <p>A process for reducing the self-adhesiveness of polytrimethy- lene terephthalate pellets comprising the steps of: contacting melt-phase-polymerised polytrimethylene terephthalate pellets (21) having an intrinsic viscosity of a least 0.4 dl/g with an aqueous liquid (29) at a temperature within the range of 65 to 100°C for a time sufficient to induce a degree of crystallinity of at least 35% in the polytrimethylene terephthalate pellets; and a crystallisation apparatus (11) for use therein.</p> <div data-bbox="860 1176 1364 1827"> </div>								

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PROCESS AND APPARATUS FOR THE CRYSTALLISATION OF  
POLYTRIMETHYLENE TEREPHTHALATE

The present invention relates to a process and apparatus for the crystallisation of polytrimethylene terephthalate.

Polytrimethylene terephthalate is a polyester useful  
5 in fibre applications in the carpet and textile industries. The manufacture of polytrimethylene terephthalate involves the condensation polymerisation of 1,3-propanediol and terephthalic acid to a polymer having an intrinsic viscosity (IV) of about 0.4 to 1.0 dl/g.

10 The polymer melt is discharged from the bottom of the melt reactor and extruded through an extrusion die into strands. The strands are quenched in cold water and cut into pellets for storage or transportation.

It has been found that polytrimethylene  
15 terephthalate pellets tend to stick together, or "block," during storage or shipping at temperatures above the polymer T<sub>g</sub> (about 45°C), which can be reached during the summer in a silo or rail car. Agglomeration of the pellets can also occur during drying using a hopper-type  
20 dryer. Agglomeration of the pellets complicates and increases the costs of handling the pellets.

It is therefore an object of the present invention to produce polytrimethylene terephthalate pellets which are resistant to blocking during storage or shipping. It  
25 is a further object to produce polytrimethylene terephthalate pellets which can be dried in a hopper without agglomeration. It is a still further object of one aspect of the invention to reduce fines production in the manufacture of polytrimethylene terephthalate.

It has now been found that partially crystallised polytrimethylene terephthalate pellets are less susceptible to blocking, and a process has been developed for partial crystallisation of polytrimethylene terephthalate pellets. It would be desirable to practise such a process in the continuous polymerisation of polytrimethylene terephthalate.

It is therefore an object of the invention to provide apparatus for crystallising polytrimethylene terephthalate pellets in a continuous polymerisation process.

According to the present invention, there is provided a process for reducing the self-adhesiveness of polytrimethylene terephthalate pellets comprising the steps of:

contacting melt-phase-polymerised polytrimethylene terephthalate pellets having an intrinsic viscosity of at least 0.4 dl/g with an aqueous liquid at a temperature within the range of 65 to 100°C for a time sufficient to induce a degree of crystallinity of at least 35% in the polytrimethylene terephthalate pellets.

The present invention further provides an apparatus for increasing the crystallinity of polytrimethylene terephthalate pellets comprising:

a vertically-elongated vessel having

(a) at its upper end, a lateral inlet for controlled introduction of polytrimethylene terephthalate pellets in transport water in vortex flow through the upper portion thereof;

(b) means in the upper interior portion of the vessel for separating the polytrimethylene terephthalate pellets from the transport water and for removing the transport water from the vessel;

(c) sides which extend vertically from the top of the vessel and, in the lower portion thereof, taper inward to form a funnel which terminates in an exit for polytrimethylene terephthalate pellets from the bottom of the vessel;

(d) an inlet for controlled introduction of a heated aqueous liquid into the funnel end of the vessel; and

(e) means for opening and closing said exit to provide controlled flow of partially-crystallised pellets therefrom.

The present invention will now be described by way of example with reference to the accompanying drawings, in which:-

FIGURE 1 is a process flow diagram of one embodiment of the polytrimethylene terephthalate preparation process of the present invention.

FIGURE 2 is a schematic flow diagram of a continuous polytrimethylene terephthalate preparation process employing the apparatus of the present invention.

FIGURE 3 is a schematic cross-sectional diagram of one embodiment of the crystallisation apparatus of the present invention.

FIGURE 4 is a differential scanning calorimetric (DSC) thermogram of a clear, as-pelletised polytrimethylene terephthalate sample, with no additional crystallisation.

FIGURE 5 is a DSC thermogram of a partially-crystallised polytrimethylene terephthalate sample which has been immersed in 80°C water for 5 seconds.

FIGURE 6 is a DSC thermogram of a well-crystallised polytrimethylene terephthalate sample which had been immersed in 80°C water for 10 seconds.

FIGURE 7 shows the effects of hot-water immersion time and temperature on the density of polytrimethylene terephthalate.

5       FIGURE 8 shows the effects of hot-water immersion time and temperature on the degree of crystallinity of polytrimethylene terephthalate.

10       The present invention involves the preparation of polytrimethylene terephthalate pellets which have improved stability against blocking at elevated temperatures.

15       In general, polytrimethylene terephthalate is prepared by reacting, at elevated temperature, a molar excess of 1,3-propanediol with terephthalic acid in a two-stage (esterification/polycondensation) process, with removal of by-product water, for a time effective to produce a polytrimethylene terephthalate having an intrinsic viscosity (measured in 60:40 phenol:tetrachloroethane at 30°C) of at least 0.4 dl/g.

20       The esterification step is carried out at a temperature within the range of 230 to 300°C, preferably 240 to 270°C, under elevated pressure, preferably under nitrogen gas, within the range of 137.8 to 1378 kPa (20 to 200 psi), preferably about 344.5 kPa (about 50 psi). Excess 1,3-propanediol and byproduct water are removed by  
25       suitable means such as overhead distillation as the esterification proceeds.

30       The esterification product, a low IV prepolymer, is then polycondensed under vacuum in the presence of a catalyst while byproduct water is removed. Suitable polycondensation catalysts include compounds of titanium or tin, such as titanium butoxide, present in an amount within the range of 10 to 400 ppm titanium or tin, based on the weight of the polymer. The polymerisation conditions are selected so as to produce a molten

polyester having a target intrinsic viscosity of at least 0.4 dl/g, preferably within the range of 0.5 to 1.0 dl/g.

The polytrimethylene terephthalate is discharged from the melt reactor and passed through an extrusion die to form polymer melt strands which are cooled and partially solidified by contact with cold water on a strand guide. The sequence of pelletisation/crystallisation is not critical. Pre-pelletising crystallisation involves immersion of polymer melt strands in hot water prior to cutting of the strands, preferably en route from the extruder to the pelletiser. The preferred method, however, for process efficiency and pellet quality, is to conduct crystallisation downstream of pelletisation.

Immediately after pelletisation, the surfaces of the pellets are solid while the cores are still partially molten. To prevent the pellets from sticking together, the pellets are flushed with additional cooling water, which completely solidifies the pellets. In the embodiment as shown in Figure 1, the pellets are transported in a water slurry 1 to a dewatering screen 2 to remove most of the water 3. The pellets 4 at this stage are clear and have a low degree of crystallinity. The pellets 4 are then collected in hopper 5, combined with an aqueous liquid 6, preferably water, which can be preheated, and conveyed as a slurry 7 to the bottom of the hot water crystallisation apparatus 8, which can be any vessel that provides agitation, the desired fluid temperature and appropriate residence time. In its simplest form, crystallisation can be carried out in an elongated conduit between the pelletiser and the pellet dryer, such as, for example, a 4-6" diameter pipe through which a hot water slurry of pellets is passed at a rate which results in the desired hot water contact time. The

slurry is passed from the crystallisation apparatus through screen 9 for water removal, and the pellets are transported to dryer 10.

5 Crystallisation of the pellets can be carried out in a batch or continuous process. For batch processes, crystallisation can be carried out in any suitable holding vessel that provides hot water agitation for adequate heat transfer and temperature control. The process is preferably carried out continuously for an efficient commercial process. Integration of crystallisation into a continuous polymerisation process requires coordination with upstream and downstream processing and careful control of pellet residence time in the crystalliser for uniform crystallisation of the pellets. For process economics, it is preferred that crystallisation be carried out on the pelletisation line, maximizing the use of residual pellet heat and eliminating the need for an additional pellet dryer.

20 In either batch or continuous crystallisation, the polytrimethylene terephthalate pellets will be immersed in hot aqueous liquid at temperatures within the range of 65 to 100°C, preferably 65 to 85°C, for a time sufficient to achieve the desired crystallinity. Said aqueous liquid is preferably water.

25 According to a preferred process, polytrimethylene terephthalate pellets exiting the pelletiser are washed with transport water onto a screen through which most of the water is drained. The pellets are then conveyed mechanically to a hot water crystallisation apparatus, which can be, for example, a vertical or horizontal liquid agitated vessel, a liquid fluidized bed, a hydraulic transfer system using hot water as the transfer medium, or a liquid moving bed providing the desired fluid temperature and residence time. A liquid moving



bed is preferred because it provides uniform residence time and uniform heating of the pellets, resulting in uniform pellet crystallinity and opacity.

5 In a preferred process, as shown in Figure 2, the pellets are transported in a water slurry 1 to a dewatering screen 2 to remove most of the water 3. The pellets at this stage are clear and have a low degree of crystallinity. The pellets 4 are then collected in hopper 5, combined with water 6, which can be preheated, and conveyed as a slurry 7 to the top of crystallisation apparatus 11. Transport water is separated from the pellets through screen 8 and passed from the crystallisation apparatus via 9. The pellets travel in plug flow through the middle portion of the vessel and into a fluidized bed of hot water introduced via 10 into the cone-shaped bottom portion of the crystallisation apparatus. Movement of the pellets in the crystallisation apparatus is controlled so as to provide the contact time required to impart polymer crystallinity of at least 35%. The slurry is passed from the crystallisation apparatus through screen 12 for water removal, and the pellets are transported via 13 to dryer 14.

25 One embodiment of a preferred crystallisation apparatus, which is designed for continuous crystallisation of polytrimethylene terephthalate pellets in a liquid moving bed, is shown in FIGURE 3.

30 A slurry 21 of polytrimethylene terephthalate pellets transported from the pelletiser in hot water is introduced tangentially for vortex flow into the upper portion of vertically-elongated crystallisation apparatus 11 via horizontally-oriented entry conduit 22. Tangential introduction of the pellet slurry permits centrifugal separation of the pellets from the water

within the interior upper portion of the apparatus. In the embodiment shown, the water passes through screen 23, into centre tube 24, and out of the tube via exit conduit 25, while the pellets rotate in a descending route along cylindrical crystallisation apparatus wall 26. The interior of the crystallisation apparatus can be fitted with baffles if desired. The descending pellets form a slow-moving bed in plug flow as they approach the middle portion 27 of the crystallisation apparatus. For optimum flow of crystallised pellets from the crystallisation apparatus, it has been found to be advantageous to have local fluidization near the bottom of the vessel, in the cone portion. This can be achieved with a total water flow rate such that the liquid velocity within the bottom cone region is well above the minimum fluidization velocity while the liquid velocity within the upper cyclindrical region of the vessel is below the minimum fluidization velocity. The speed of downward movement of the pellet bed is dependent on the speed of pellet discharge at the lower end 28 of the vessel and the flow of incoming hot water stream 29 from a water surge vessel (not shown) into the crystallisation apparatus via hot water inlet 30. The incoming water temperature will be within the range of 65 to 100°C, preferably 65 to 85°C. As the flow of the descending pellets slows, the concentration of pellets in the lower portion of the vessel increases. Because of the low effective pellet weight (pellet weight less liquid buoyancy), the lubricating action of the water, the fast crystallisation of polytrimethylene terephthalate and the low crystallisation temperatures required, no agglomeration of pellets will occur in the crystallisation apparatus so long as continuous movement of the pellets is maintained in the liquid in the lower portion of the vessel. The

crystallised pellets exit the bottom of the cone and are passed via 31 to drying and further processing.

The crystallisation apparatus will typically have an operating pressure of 0 to 34.5 kPa (0 to 5 psig). The size of the apparatus will depend upon the operating variables and overall plant capacity. A typical hot water crystallisation apparatus in a commercial plant would be in the general range of 1.82 to 3.04 m (6 to 10 feet) in length, with the cone portion being 0.45 to 0.61 m (1.5 to 2 feet) of that total length. The pellet residence time will typically range from 30 seconds to 5 minutes.

The flow of the pellets through the crystallisation apparatus will thus approximately define three regions. In the upper half of the apparatus the concentration of pellets will be relatively dilute, with pellet concentration increasing below this level to form a moving bed of pellets in plug flow downward through the lower portion of the vessel at a volume concentration of approximately 50 to 70 percent. In the lower portion of the cone near the vessel exit, the entering hot water, introduced at a velocity to keep the pellets suspended, forms a fluidized bed of relatively dilute pellet volume concentration of approximately 40%. This local fluidization in the conical area is desirable to facilitate continuous discharge of the crystallised pellets from the vessel. This can be achieved by use of a total water flow rate such that the liquid velocity within the bottom cone region is well above the minimum fluidization velocity, while the liquid velocity within the intermediate region of the vessel is below the minimum fluidization velocity.

To ensure that the pellets are sufficiently crystallised to prevent blocking, it is desirable to

crystallise the pellets to the extent that the product has a DSC thermogram characterised by the absence of a cold crystallisation peak (see Figs. 4 - 6). The imparted degree of crystallisation is related to the starting polymer density and IV, the temperature of the aqueous liquid and the length of time the polymer is immersed in the aqueous liquid. Said aqueous liquid is preferably water. The following chart provides general guidance on immersion times required to achieve at least 35% crystallinity (for non-delustered polytrimethylene terephthalate) over the temperature range of 60 to 100°C.

	<u>Water Temperature (°C)</u>	<u>Crystallisation Time</u>
	60	20 minutes
	65	3 minutes
15	70	30 seconds
	80	10 seconds
	90	5 seconds
	100	3 seconds

For commercial operation, the desirability of faster crystallisation must be balanced against the cost of maintaining higher water temperatures. The upper temperature is also limited by the tendency of polytrimethylene terephthalate to undergo hydrolytic degradation (detected as a decrease in intrinsic viscosity) at temperatures above about 100°C. For process efficiency and economics, the preferred water temperature is within the range of 65 to 85°C and the polymer is immersed for no longer than 3 minutes, preferably for a time within the range of 3 seconds to 3 minutes, with delustered polymer generally requiring longer immersion than non-delustered polymer.

After the selected residence time in the crystallisation apparatus, the pellet/water slurry is

discharged into a pellet dryer. The pellets are cooled to a temperature below 60°C, either by cold water quench en route to the dryer or, if the dryer environment is sufficiently cool, in the dryer itself.

5 Polytrimethylene terephthalate pellets treated by the process and/or the crystallisation apparatus of the present invention will preferably have an opaque appearance and typically exhibit the following physical properties:

10 density of at least 1.33 g/cm<sup>3</sup>;  
crystallinity of at least 35%;  
Tg of at least 60°C;  
apparent crystallite size of at least 10 nm,  
preferably in the range of 10 to 13 nm.

15 As used herein, "crystallinity" indicates the degree of crystallisation and refers to an increase in the crystalline fraction and a decrease in the amorphous fraction of the polymer. In general, a crystallinity of at least 35%, preferably within the range of 36 to 45%,  
20 measured as described below, is desired. The calculation of crystallinity herein is based on the relationship of volume fractional crystallinity ( $X_c$ ) of a sample to the density ( $D_s$ ) of the sample:

$$X_c = (D_s - D_a) / (D_c - D_a)$$

25 where  $D_a$  is the density of amorphous polytrimethylene terephthalate (= 1.295 g/cm<sup>3</sup>) and  $D_c$  is the density of polytrimethylene terephthalate crystal (= 1.387 g/cm<sup>3</sup>). The weight fractional crystallinity,  $S_w$ , equals  $(D_c/D_s)/X_c$ . Crystallinity can also be estimated from a

DSC thermogram, but it has been found that the described density method provides more consistent results, and this method has therefore been chosen for calculation of fractional crystallinity herein.

5           The process and apparatus of the present invention each overcome the problem of polytrimethylene terephthalate pellets adhering together during hot-weather storage or transportation, and enables drying of the pellets in a hopper-type dryer prior to melt  
10           processing or solid-state polymerisation. The process and apparatus of the present invention also assist in reducing fines which can be generated in the manufacture and processing of polytrimethylene terephthalate. The apparatus employs a liquid moving bed for uniform  
15           residence time and uniform heating of the pellets, resulting in uniform pellet crystallinity and opacity.

          The resulting partially-crystallised polytrimethylene terephthalate pellets can be spun into fibres or made into film or engineering thermoplastics.

20           Example 1

Hot-Water Crystallisation of Amorphous Polytrimethylene Terephthalate. Clear pellets of polytrimethylene terephthalate (total weight 5g) having an IV of 0.904 dl/g, a degree of polymerisation (DP) of about 102, and a  
25           weight per pellet of about 0.02g were placed in a wire mesh basket. The basket was placed in a 4L beaker filled with water heated to a constant temperature (as indicated in Table 1) between 50 and 100°C for a time ranging from 3 seconds to 30 minutes. The water was vigorously stirred  
30           over the time of immersion. The basket was removed from the hot water and immediately immersed in iced water to stop crystallisation. After drying in the room environment, each sample was tested as described below and the appearance of each sample was noted. Test

results are shown in Table 1. Selected samples were also measured by wide angle x-ray diffraction (WAXD) to determine apparent crystallite size (ACS).

The IV of each treated sample was determined in 60:40 phenol:tetrachloroethane solvent at 30°C. A drop in IV indicates hydrolytic degradation during crystallisation in hot water. As can be seen in Table 1, significant IV drops occurred only under the more severe crystallisation conditions (e.g., 10 minutes or longer in 90°C water and 5 minutes or longer in 100°C water).

Each sample was scanned on a differential scanning calorimeter (DSC) at a rate of 10°C per minute. Useful DSC data included T<sub>g</sub>, heat of fusion and heat of crystallisation. From the difference between the heat of fusion and the heat of crystallisation on the thermogram, the fractional crystallinity by weight, S<sub>w</sub>, of the sample was calculated using 146 J/g for the heat of fusion for crystalline polytrimethylene terephthalate. Figures 4, 5 and 6 are DSC thermograms for 3 samples having different degrees of crystallisation.

Figure 4 shows a DSC thermogram for a clear, as-pelletised polytrimethylene terephthalate sample. It shows a T<sub>g</sub> inflection at 45°C, a cold crystallisation peak with a peak temperature (T<sub>m</sub>) at 68.9°C, and a fusion peak with a peak temperature (T<sub>c</sub>) at 229.4°C. From the heat of fusion and heat of crystallisation, the crystallinity of the sample was calculated to be 20.4% based on DSC.

Figure 5 shows a DSC thermogram of a pelletised polytrimethylene terephthalate sample that had been immersed in 80°C water for 5 seconds. This DSC thermogram has a smaller cold crystallisation peak than the DSC thermogram in Figure 4, reflecting the increased crystallinity of the sample (28.2%). The existence of

the cold crystallisation peak indicates that crystallisation of this sample was incomplete. The T<sub>g</sub> of the sample had increased to 48.3°C as a result of its increased crystallinity.

5        Figure 6 is a DSC thermogram of a pelletised polytrimethylene terephthalate sample that had been immersed in 80°C water for 10 seconds. This DSC thermogram does not show a distinct cold crystallisation exotherm, indicating that the sample was well  
10        crystallised. From the heat of fusion, the crystallinity of the sample was estimated to be 40.5%. The T<sub>g</sub> of the sample was increased to 61.6°C by the crystallisation.

      The density of each sample was determined in a density gradient column. From the density, the  
15        crystallinity was calculated using 1.295 g/cm<sup>3</sup> for the density of amorphous polytrimethylene terephthalate and 1.387 g/cm<sup>3</sup> for the density of polytrimethylene terephthalate crystal.

      The apparent crystallite size of selected samples  
20        was determined using wide-angle x-ray diffraction measurements. Although the polymer pellets before hot-water treatment had some degree of crystallinity, the crystallites were too small to be detected by WAXD. After hot-water crystallisation, the crystallites were  
25        large enough to be measured and ranged generally from about 10 to about 13 nm.

      Figure 7 shows the effects of hot-water immersion time and temperature on the density of polytrimethylene terephthalate.

30        Figure 8 shows the effects of hot-water immersion time and temperature on the degree of crystallinity of polytrimethylene terephthalate.



TABLE 1  
Hot Water Crystallisation Data for Polytrimethylene terephthalate

Water Temp. (°C)	Cryst. Time	Density (g/cm <sup>3</sup> )	% Crystallinity		DSC Cold Cryst heat (J/g)	Appearance	IV (dl/g)
			Density	DSC			
NA (Control)	none	1.3074	13.5	20.4	25.3	Clear	0.904
50	5 min	1.3076	13.7	22.6	23.6	Clear	0.902
50	10 min	1.3078	13.9	21.7	22.1	Clear	0.906
50	30 min	1.3130	19.6	29.9	13.4	Clear	0.903
55	30 sec	1.3078	13.9	24.2	22.1	Clear	
55	1 min	1.3080	14.1	20.2	23.1	Clear	
55	5 min	1.3100	16.3	26.3	19.2	Clear	0.908
55	7 min	1.3137	20.3	24.5	15.1	Hazy	0.910
55	10 min	1.3167	23.6	26.2	9.2	Hazy	0.903
55	20 min	1.3234	30.9	34.3	5.2	Translucent	0.906
60	30 sec	1.3085	14.7	21.0	24.5	Clear	
60	1 min	1.3092	15.4	23.0	22.9	Hazy	
60	3 min	1.3130	19.6	32.4	7.1	Translucent	
60	5 min	1.3250	32.6	31.6	3.8	Translucent	0.906
60	7 min	1.3262	33.9	33.3	3.2	Translucent	0.908
60	10 min	1.3266	34.3	33.1	2.5	Opaque	0.906

TABLE 1 (Cont'd)									
Hot Water Crystallisation Data for Polytrimethylene terephthalate									
Water Temp. (°)	Cryst. Time	Density (g/cm <sup>3</sup> )	% Crystallinity		DSC Cold Cryst heat (J/g)	Appearance	IV (dl/g)		
			Density	DSC					
60	20 min	1.3269	34.6	34.9	1.8	Opaque	0.909		
65	15 sec	1.3085	14.7	23.0	11.8	Clear			
65	30 sec	1.3180	25.0	29.8	1.5	Hazy			
65	1 min	1.3262	33.9	31.5	0.8	Translucent	0.906		
65	3 min	1.3283	36.2	36.0	0	Opaque	0.907		
65	5 min	1.3289	36.8	37.7	0	Opaque	0.908		
65	10 min	1.3291	37.1	36.3	0	Opaque	0.904		
65	20 min	1.3293	37.3	36.9	0	Opaque	0.905		
70	5 sec	1.3079	14.0	22.3	24.5	Clear			
70	10 sec	1.3100	16.3	21.1	20.8	Hazy			
70	15 sec	1.3214	28.7	29.8	10.7	Translucent			
70	30 sec	1.3282	36.1	37.5	0	Opaque			
70	1 min	1.3287	36.6	36.8	0	Opaque	0.906		
70	3 min	1.3295	37.5	35.8	0	Opaque	0.907		
70	5 min	1.3300	38.0	38.0	0	Opaque	0.907		
70	7 min	1.3304	38.5	38.6	0	Opaque	0.906		

TABLE 1 (Cont'd)  
Hot Water Crystallisation Data for Polytrimethylene terephthalate

Water Temp. (°)	Cryst. Time	Density (g/cm <sup>3</sup> )	% Crystallinity		DSC Cold Cryst heat (J/g)	Appearance	IV (dl/g)
			Density	DSC			
70	10 min	1.3307	38.8	37.9	0	Opaque	0.902
70	20 min	1.3307	38.8	37.6	0	Opaque	0.905
80	3 sec	1.3120	18.5	26.1	19.2	Hazy	
80	5 sec	1.3145	21.2	24.0	20.6	Translucent	
80	10 sec	1.3295	37.5	40.5	0	Opaque	
80	15 sec	1.3307	38.8	38.6	0	Opaque	
80	30 sec	1.3310	39.1	39.1	0	Opaque	
80	1 min	1.3315	39.6	35.4	0	Opaque	0.902
80	3 min	1.3323	40.5	39.5	0	Opaque	0.904
80	5 min	1.3326	40.9	37.9	0	Opaque	0.905
80	7 min	1.3327	40.9	40.7	0	Opaque	0.903
80	10 min	1.3326	40.9	39.8	0	Opaque	0.904
80	20 min	1.3329	40.9	38.7	0	Opaque	0.903
90	3 sec	1.3200	27.2	29.9	12.4	Translucent	
90	5 sec	1.3304	38.5	36.3	0	Opaque	
90	10 sec	1.3310	39.1	36.6	0	Opaque	
90	15 sec	1.3315	39.7	37.8	0	Opaque	

TABLE 1 (Cont'd)									
Hot Water Crystallisation Data for Polytrimethylene terephthalate									
Water Temp. (°)	Cryst. Time	Density (g/cm <sup>3</sup> )	% Crystallinity		DSC Cold Cryst heat (J/g)	Appearance	IV (dl/g)		
			Density	DSC					
90	30 sec	1.3320	40.2	36.1	0	Opaque			
90	1 min	1.3325	40.8	37.6	0	Opaque	0.904		
90	3 min	1.3330	41.3	37.0	0	Opaque	0.905		
90	5 min	1.3332	41.5	38.9	0	Opaque	0.903		
90	7 min	1.3335	41.8	40.1	0	Opaque	0.904		
90	10 min	1.3337	41.8	39.8	0	Opaque	0.903		
90	20 min	1.3336	42.0	40.5	0	Opaque	0.900		
100	3 sec	1.3318	40.0	30.1	0	Opaque			
100	5 sec	1.3323	40.5	36.3	0	Opaque			
100	10 sec	1.3327	41.0	36.7	0	Opaque			
100	15 sec	1.3330	41.3	40.0	0	Opaque			
100	30 sec	1.3335	41.8	35.6	0	Opaque			
100	1 min	1.3338	42.2	38.5	0	Opaque	0.903		
100	3 min	1.3342	42.6	27.7	0	Opaque	0.901		
100	5 min	1.3344	42.8	41.6	0	Opaque	0.898		
100	7 min	1.3345	42.9	37.7	0	Opaque	0.894		
100	10 min	1.3345	42.9	39.8	0	Opaque	0.897		

TABLE 1 (Cont'd)  
Hot Water Crystallisation Data for Polytrimethylene terephthalate

Water Temp. (°)	Cryst. Time	Density (g/cm <sup>3</sup> )	% Crystallinity		DSC Cold Cryst heat (J/g)	Appearance	IV (dl/g)
			Density	DSC			
100	20 min	1.3347	43.2	40.2	0	Opaque	0.898
80	3 sec	1.3120	18.5	26.1	19.2	Hazy	
80	5 sec	1.3145	21.2	24.0	20.6	Translucent	
80	10 sec	1.3295	37.5	40.5	0	Opaque	
80	15 sec	1.3307	38.8	38.6	0	Opaque	
80	30 sec	1.3310	39.1	39.1	0	Opaque	
80	1 min	1.3315	39.6	35.4	0	Opaque	0.902
80	3 min	1.3323	40.5	39.5	0	Opaque	0.904
80	5 min	1.3326	40.9	37.9	0	Opaque	0.905
80	7 min	1.3327	40.9	40.7	0	Opaque	0.903
80	10 min	1.3326	40.9	39.8	0	Opaque	0.904
80	20 min	1.3329	40.9	38.7	0	Opaque	0.903
90	3 sec	1.3200	27.2	29.9	12.4	Translucent	
90	5 sec	1.3304	38.5	36.3	0	Opaque	
90	10 sec	1.3310	39.1	39.6	0	Opaque	
90	15 sec	1.3315	39.7	27.8	0	Opaque	
90	30 sec	1.3320	40.2	36.1	0	Opaque	

TABLE 1 (Cont'd)									
Hot Water Crystallisation Data for Polytrimethylene terephthalate									
Water Temp. (°)	Cryst. Time	Density (g/cm <sup>3</sup> )	% Crystallinity		DSC Cold Cryst heat (J/g)	Appearance	IV (dl/g)		
			Density	DSC					
90	1 min	1.3325	40.8	37.6	0	Opaque	0.904		
90	3 min	1.3330	41.3	37.0	0	Opaque	0.905		
90	5 min	1.3332	41.5	38.9	0	Opaque	0.903		
90	7 min	1.3335	41.8	40.1	0	Opaque	0.904		
90	10 min	1.3337	41.8	39.8	0	Opaque	0.903		
90	20 min	1.3336	42.0	40.5	0	Opaque	0.900		
100	3 sec	1.3318	40.0	30.1	0	Opaque			
100	5 sec	1.3323	40.5	36.3	0	Opaque			
100	10 sec	1.3327	41.0	36.7	0	Opaque			
100	15 sec	1.3330	41.3	40.0	0	Opaque			
100	30 sec	1.3335	41.8	35.6	0	Opaque			
100	1 min	1.3338	42.2	38.5	0	Opaque	0.903		
100	3 min	1.3342	42.6	27.7	0	Opaque	0.901		
100	5 min	1.3344	42.8	41.6	0	Opaque	0.898		
100	7 min	1.3345	42.9	37.7	0	Opaque	0.894		
100	10 min	1.3345	42.9	39.8	0	Opaque	0.897		
100	20 min	1.3347	43.2	40.2	0	Opaque	0.898		

C L A I M S

1. A process for reducing the self-adhesiveness of polytrimethylene terephthalate pellets comprising the steps of:

5       contacting melt-phase-polymerised polytrimethylene terephthalate pellets having an intrinsic viscosity of at least 0.4 dl/g with an aqueous liquid at a temperature within the range of 65 to 100°C for a time sufficient to induce a degree of crystallinity of at least 35% in the polytrimethylene terephthalate pellets.

10      2. The process according to claim 1 in which the polytrimethylene terephthalate pellets having an intrinsic viscosity within the range of 0.5 to 1.0 dl/g.

15      3. The process according to claim 1 or 2 in which the polytrimethylene terephthalate pellets are maintained in contact with the aqueous liquid for a time within the range of 3 seconds to 3 minutes.

4. The process according to claim 1, 2 or 3 which further comprises providing continuous pellet movement during contact with the aqueous liquid.

20      5. The process according to any one of the preceding claims in which the pellets are contacted with the aqueous liquid for a sufficient time to produce polytrimethylene terephthalate pellets having a glass transition temperature of at least 60°C.

25      6. The process according to any one of the preceding claims in which the polytrimethylene terephthalate pellets have a differential scanning calorimeter thermogram characterised by the absence of a cold crystallisation peak.

7. The process according to any one of the preceding claims in which the crystallinity of the treated polytrimethylene terephthalate pellets is within the range of 36 to 45%.

5 8. The process according to any one of the preceding claims in which the treated polytrimethylene terephthalate pellets have an apparent crystallite size of at least 10 nm.

9. The process according to any one of the preceding  
10 claims in which the polytrimethylene terephthalate pellets have a density of at least  $1.33 \text{ g/cm}^3$ .

10. Apparatus for increasing the crystallinity of polytrimethylene terephthalate pellets comprising:

a vertically-elongated vessel having

15 (a) at its upper end, a lateral inlet for controlled introduction of polytrimethylene terephthalate pellets in transport water in vortex flow through the upper portion thereof;

(b) means in the upper interior portion of the  
20 vessel for separating the polytrimethylene terephthalate pellets from the transport water and for removing the transport water from the vessel;

(c) sides which extend vertically from the top of the vessel and, in the lower portion thereof, taper  
25 inward to form a funnel which terminates in an exit for polytrimethylene terephthalate pellets from the bottom of the vessel;

(d) an inlet for controlled introduction of a heated aqueous liquid into the funnel end of the vessel;  
30 and

(e) means for opening and closing said exit to provide controlled flow of partially-crystallised pellets therefrom.



Fig.1.

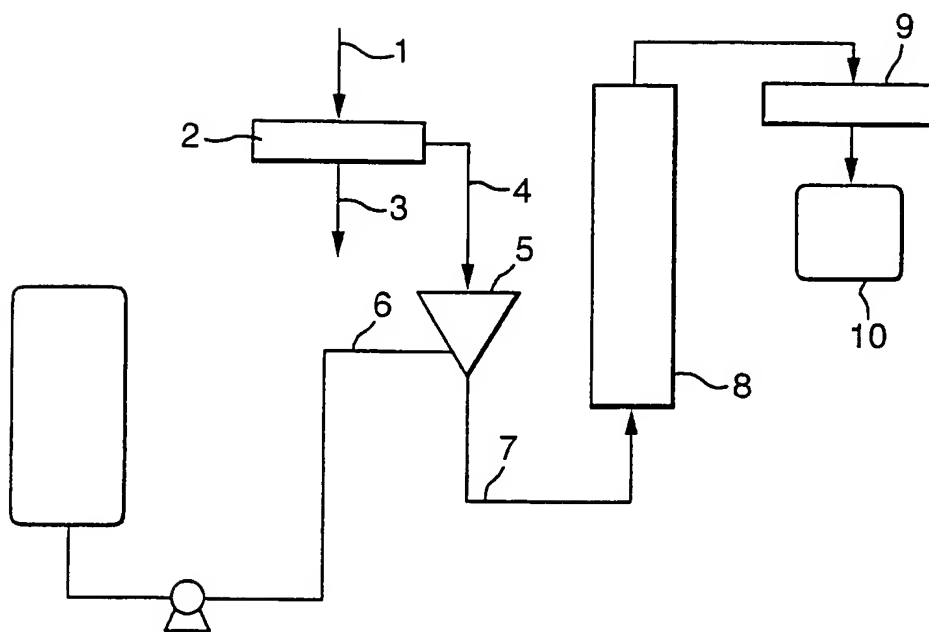
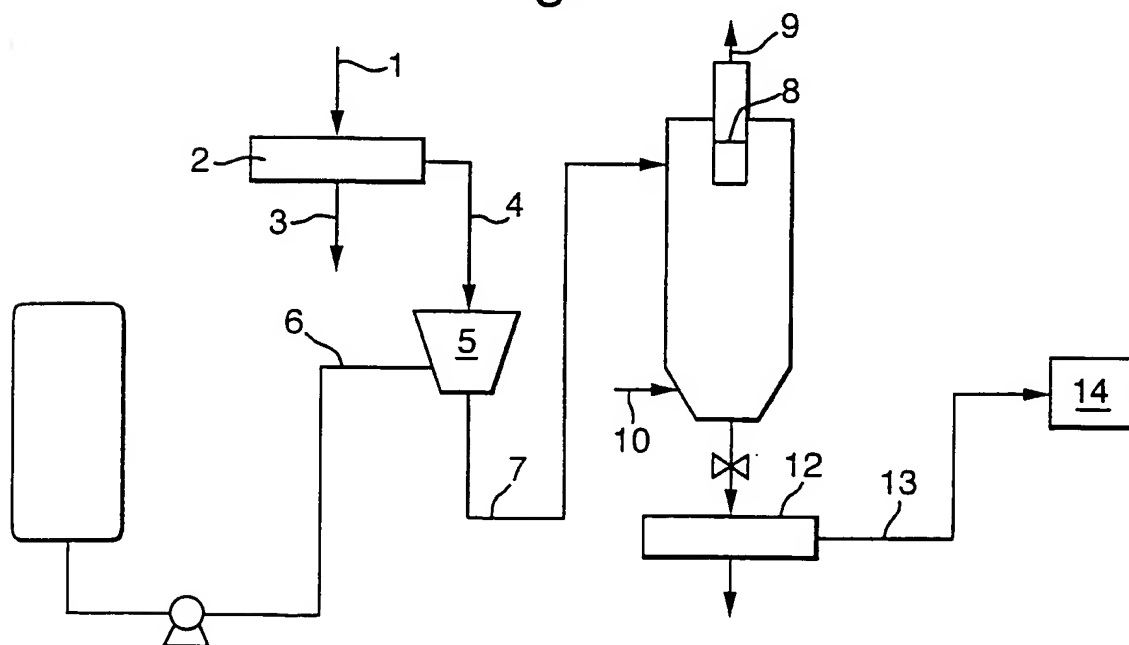


Fig.2.



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Fig.3.

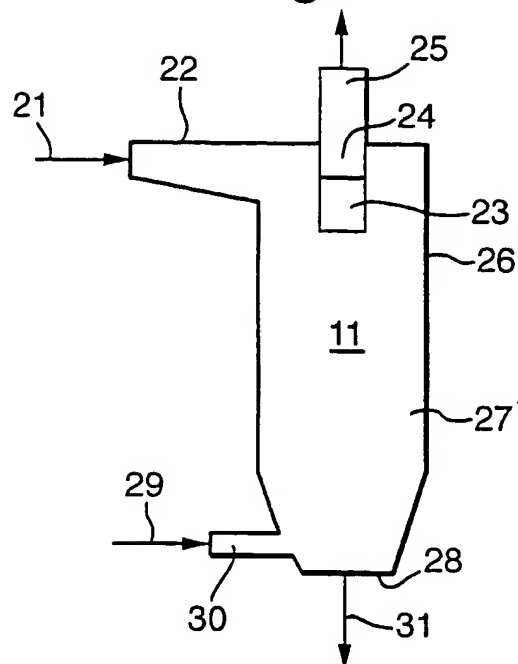
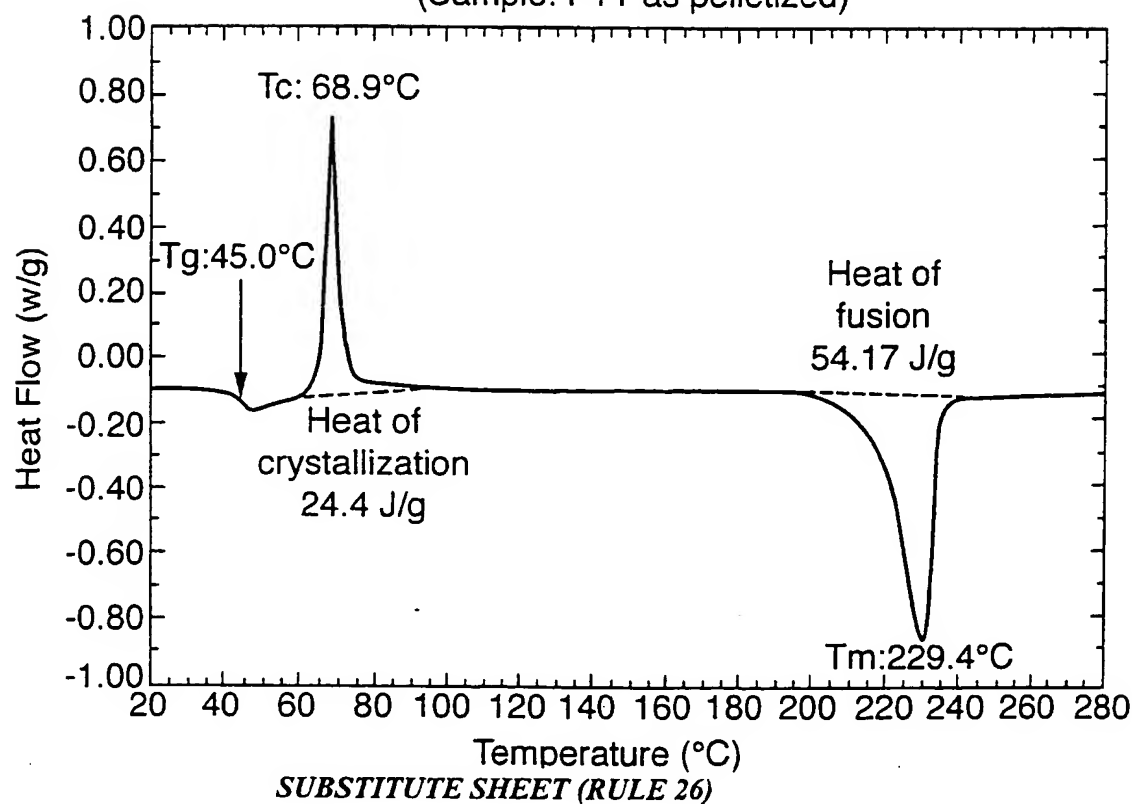


Fig.4.

DSC Thermogram of Clear PTT Pellet  
(Sample: PTT as pelletized)



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Fig.5.

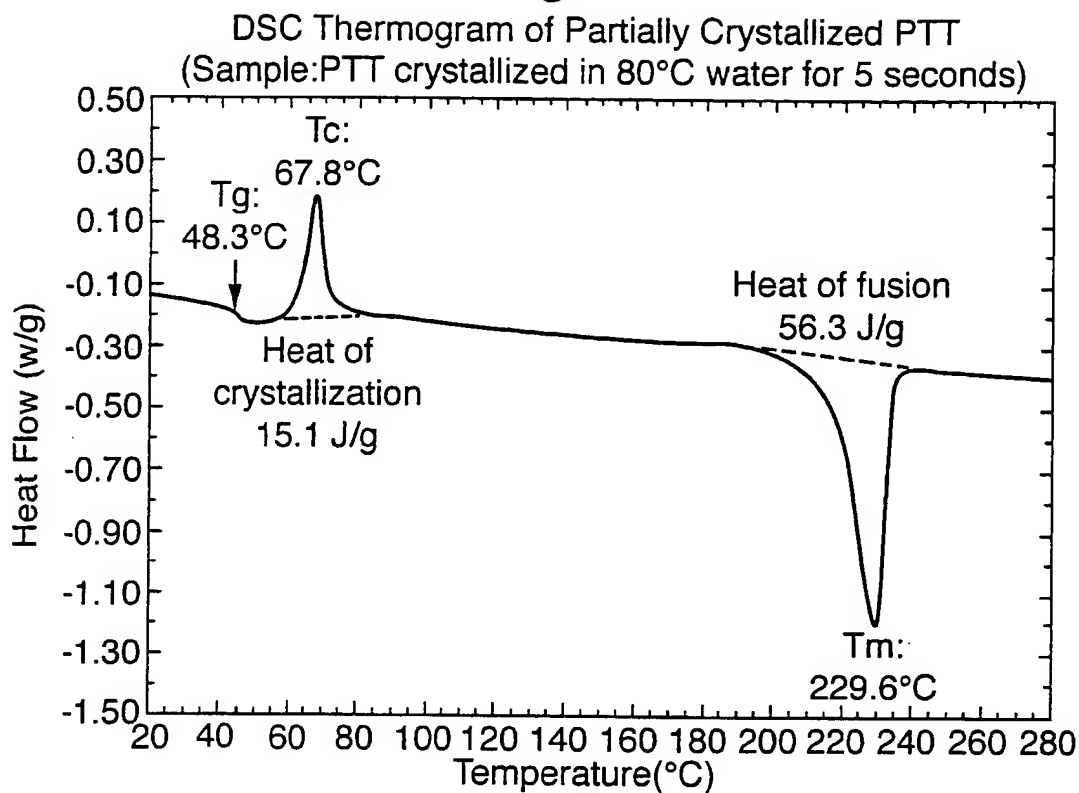


Fig.6.

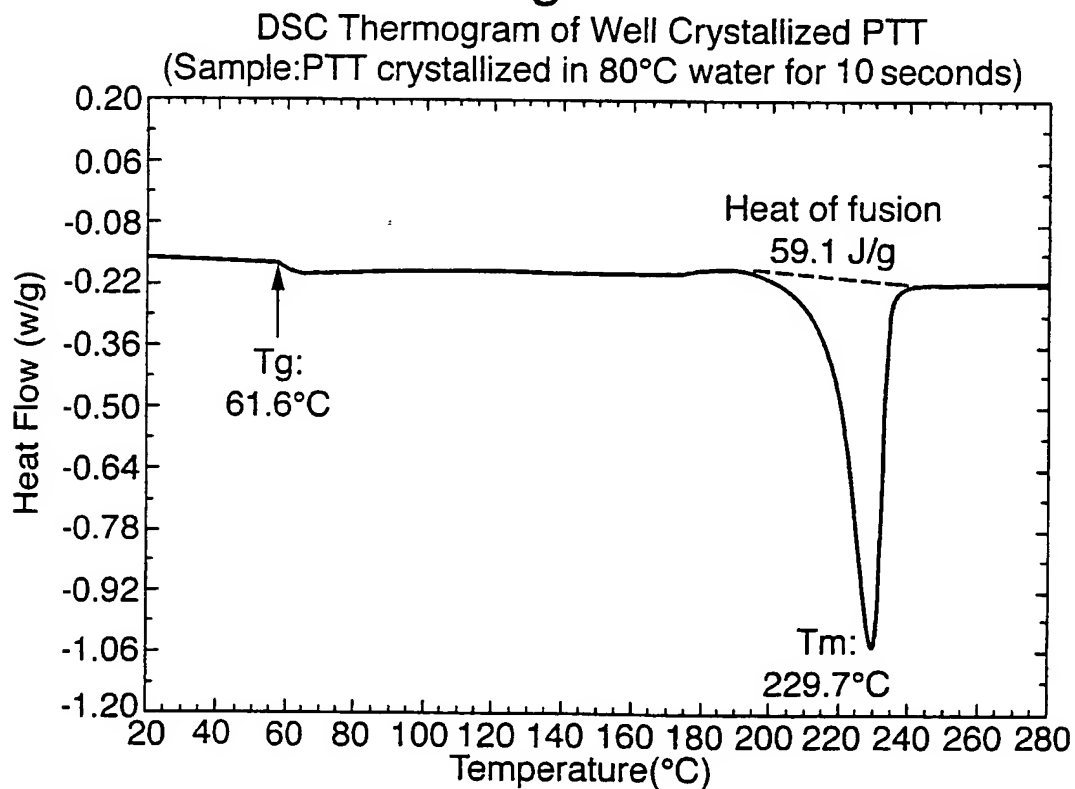
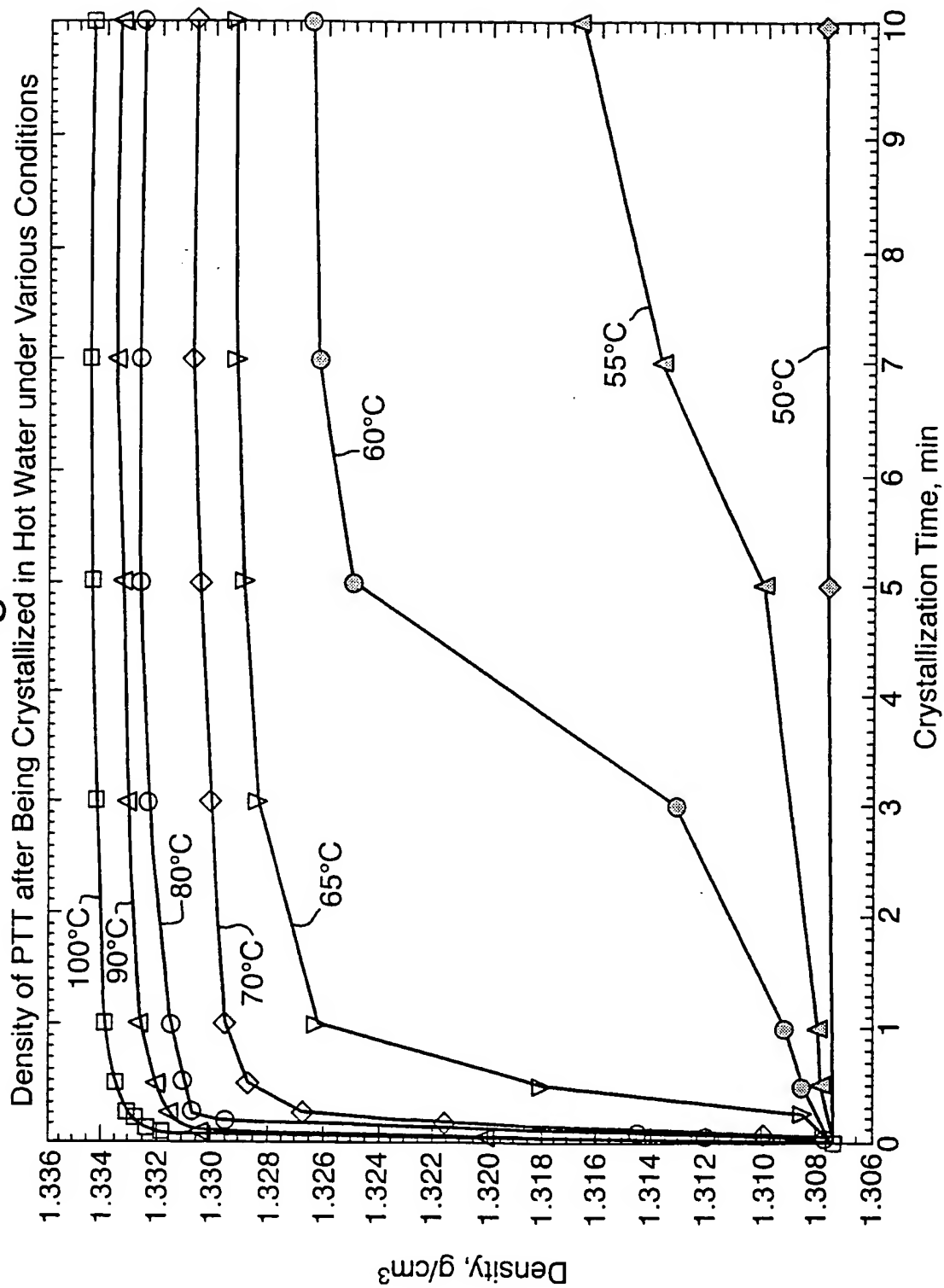


Fig. 7.



**Fig.8.**  
Crystallinity of PTT after Being Crystallized in Hot Water  
under Various Conditions

